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NITROUS OXIDE (N₂O) EMISSIONS FROM BIOTRICKLING FILTERS USED FOR AMMONIA REMOVAL AT LIVESTOCK FACILITIES

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ABSTRACT

Recently several manufacturers of nitrifying biotrickling filters for ammonia (NH₃) removal at animal house have started to add a denitrification step to the system, aiming to reduce the amount of discharge water. The aim of this research was to determine the removal efficiency of NH₃, odor and dust (PM₁₀) and to quantify the possible nitrous oxide (N₂O) formation in three of these systems that were operated on farm-scale. The average NH₃ removal efficiency that was found for the three locations was 85%, 71% and 86%, respectively. The average odor removal efficiency was 21%, 32% and 48%, respectively. The average PM₁₀ removal efficiency was 60%, 38% and 69%, respectively. The average empty bed air residence time was 0.71 s, 3.0 s and 3.6 s, respectively. All installations were successful in reducing the amount of discharge water. However, a significant part of the NH₃-N removed from the inlet air was not converted to N₂ but to N₂O, which is a potent greenhouse gas. The part of the inlet NH₃-N that was converted to N₂O-N amounted to 13%, 41%, and 24%, respectively. Further research is necessary to explore how process conditions can be adjusted in order to reduce the production and emission of N₂O.

biotrickling filter, livestock, animal house, ammonia (NH₃), denitrification, nitrous oxide (N₂O), odor

INTRODUCTION

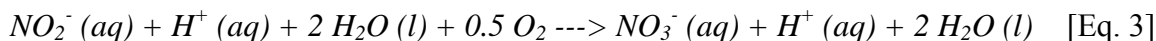
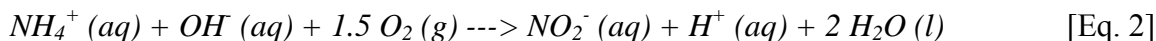
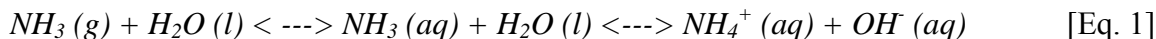
General description

Intensive livestock production is connected with a number of environmental effects which include ammonia emissions from animal houses. One of the available emission mitigation techniques for intensive livestock production is cleaning of the exhaust air of mechanically ventilated animal houses (Ndegwa et al., 2008; Melse et al., 2009a). In several European countries like the Netherlands and Germany trickling filters or air scrubbers are applied on a large scale for ammonia and odor removal in order to comply with current regulations (Arends et al., 2008; Hahne, 2011; Melse et al., 2009b). In about 90% of the cases acid scrubbers are applied and in about 10% of the cases biotrickling filters (sometimes also referred to as bioscrubbers). Besides ammonia, also part of the odor and particulate matter (PM₁₀) is removed from the air (Melse and Ogink, 2005; Melse et al., 2012b). PM₁₀ (also called thoracic particles) represents particles that have an aerodynamic diameter smaller than 10 µm.

Biotrickling filter for ammonia removal

A biotrickling filter is a packed-bed air scrubber in which bacteria are responsible for ammonia removal. The packing material usually has a large porosity, or void volume, and a large specific area. Water is distributed on top of the packed bed which is consequently wetted. Contaminated air is introduced, either horizontally (cross-current) or upwards (counter-current), resulting in intensive contact between air and water enhancing mass transfer from gas to liquid phase. Usually a fraction of the trickling water is continuously recirculated using a recirculation tank; another fraction is discharged and replaced by fresh water. The bacterial population, or biomass, in the system grows partly as a film on the packing material and is partly suspended in the water that is being recirculated.

The ammonia dissolves in a scrubbing liquid and is converted to nitrite (or nitrous acid) and subsequently to nitrate (or nitric acid) by a two step bacterial oxidation. This process is called nitrification. Usually the scrubbing liquid is recirculated. In equation 1 - 3 the mass transfer, dissociation and oxidation of ammonia are described:



As both free ammonia (NH_3) and free nitrous acid (HNO_2) may inhibit the nitrification process (Anthonisen et al., 1976; Juhler et al., 2009; Ottosen et al., 2011) nitrogen concentrations in the water are kept low by regular discharge of the recirculation liquid, as discharging water removes the accumulated nitrite and nitrate from the system. Under normal operational conditions the pH of the recirculation water is between 6.5 and 7.5 and N-total is between about 3 - 4 g.L⁻¹ (Melse and Ogink, 2005) which equals an electrical conductivity (EC) of 15 - 20 mS.cm⁻¹ (Melse et al., 2012a).

Denitrification for treatment of discharge water

One of the drawbacks of a biotrickling filter as described above is that a relatively large amount of discharge water is produced, about 10 times as much as for an acid scrubber, as the nitrogen content of the water may not exceed 3 - 4 g.L⁻¹. Current disposal costs in The Netherlands are about EUR 15 per m³ of discharge water if application on the user's own land is not possible, which is very often the case, but the discharge water must be applied to arable land of a third party.

In order to reduce the amount of discharge water several biotrickling filter manufacturers have introduced an additional denitrification treatment step. After converting ammonia to nitrate in the nitrification step, the denitrification treatment aims to subsequently convert part of the nitrate to di-nitrogen gas that is emitted as such. For successful denitrification anaerobic conditions and the presence of an electron-donor or carbon source (e.g. molasses or methanol) are required. To some extent, denitrification might already occur in a biotrickling filter without extra denitrification step as anaerobic conditions may locally occur inside the biofilm on the packing material or in the recirculation vessel. In Figure 1 a schematic of such a biotrickling system is shown.

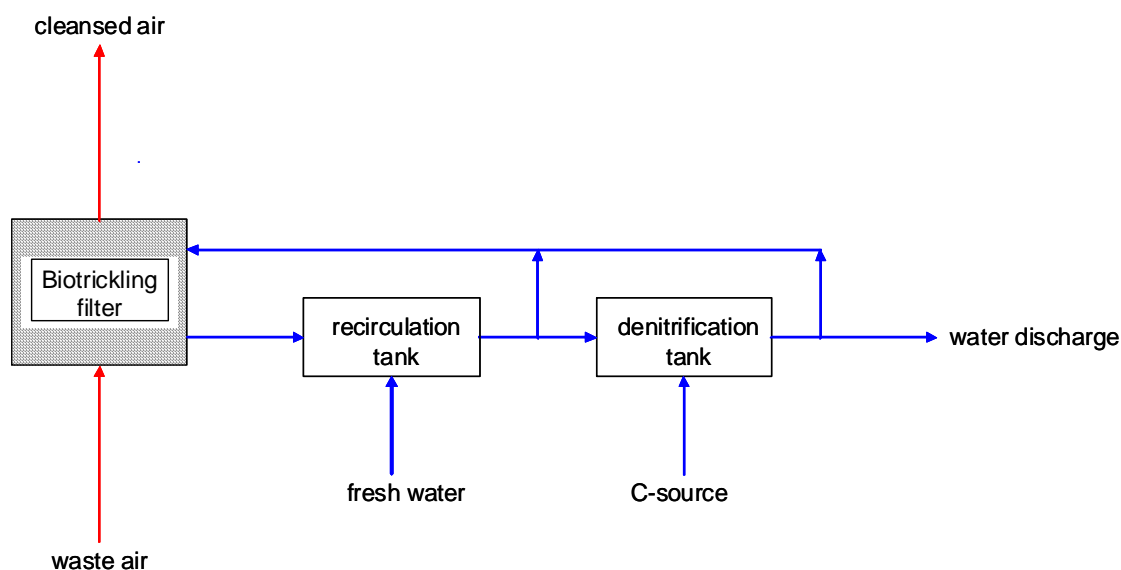
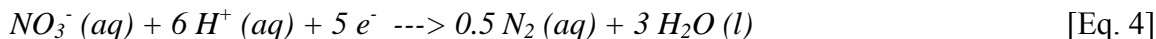


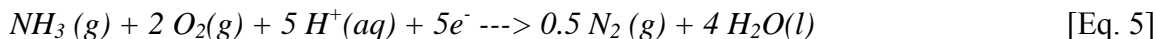
Figure 1. Schematic of biotrickling filter with denitrification of discharge water.

As a result of denitrification, only a small part of the nitrogen needs to be removed from the system with the discharge water (as NH_4^+ , NO_2^- and NO_3^-) resulting in large reduction of the water discharge rate as compared to a standard biotrickling filter without denitrification.

The denitrification process can be described as follows:



The overall reaction of the ammonia removal by nitrification and denitrification can then be described as:



However, it is known that during incomplete nitrification and denitrification in biotrickling filters some nitrous oxide (N_2O) may be produced as a by-product, which is a potent greenhouse gas (Hahne and Vorlop, 2004; Trimborn, 2006). The Global Warming Potential (GWP) of N_2O equals 298 which means that 1 kg of N_2O has the same impact as 298 kg of CO_2 on a time horizon of 100 years (IPPC, 2007).

Objectives

Currently several manufacturers of biotrickling filters for ammonia emission abatement at animal houses in The Netherlands are developing a biotrickling filter that includes a denitrification step, aiming to reduce the amount of discharge water. However, Dutch legislation does not allow the application of denitrification systems at biotrickling filters at animal houses. The aim of this research was to determine the removal efficiency of NH_3 , odor and dust (PM_{10}) and to quantify the possible N_2O formation in these denitrification systems. The measurement program was commissioned by the Dutch government.

MATERIALS AND METHODS

General description

At three farm locations a measuring program was carried out throughout one year in order to monitor the performance of a farm-scale operated biotrickling filter system with additional denitrification step. Every two months a measurement was done of ammonia, odor, nitrous oxide, methane, carbon dioxide, and particulate matter (PM_{10}) concentrations in the inlet and outlet air of the biotrickling filter. Also the ventilation rate was determined. Finally, the recirculation and discharge water was sampled and analyzed for pH, electrical conductivity (EC), and concentration of NH_4^+ , NO_2^- , NO_3^- and N-total. In Table 1 the main characteristics of the biotrickling filter locations are summarized.

Table 1. Main characteristics of packed-bed biotrickling filters treating exhaust air of animal houses.

Location	Animal number and category	Maximum ventilation rate ($\text{m}^3 \cdot \text{h}^{-1}$)	Flow configuration	Packing volume (m^3)	Packing thickness (m)
#1	30,000 broilers	75,000	cross-current	7.5	0.38
#2	45,000 broilers	125,000	cross-current	19.8	0.45
#3	2,600 fattening pigs	160,000	counter-current	72	0.90

Ammonia measurement

The ammonia measurement were carried out in duplicate with the impinger method. In this method a small amount of air is continuously drawn at a fixed flow rate which is controlled by a critical orifice ($1 \text{ L} \cdot \text{min}^{-1}$) through a pair of impingers (0.5 L each), connected in series, containing a strong acid solution (nitric acid, 0.03 - 0.2 M). NH_3 is trapped by the acid and accumulates in the bottles during 24 hours. The values of the sampling flow rate and nitric acid concentration are chosen so that the second

impinger, which serves as a control, does not contain more than 5% of the amount of NH_3 trapped in the first impinger. All sampling tubes have been made of Teflon to prevent adsorption of NH_3 . Finally, the NH_3 concentration of the air is calculated from the nitrogen content of the acid solution in the bottles, which is determined spectrophotometrically (NNI, 1998), and the air sampling flow rate.

Odor measurement

For odor measurement, an air sample was collected in an initially evacuated 40 L Nalophane (PET) bag for 2 hours between 10:00 and 12:00. The air sampling flow rate was controlled by a critical orifice ($400 \text{ ml} \cdot \text{min}^{-1}$). The bag is placed in an airtight container, the inlet of the bag is connected to the sampling port of the air inlet or air outlet of the scrubber and the bag is filled by creating an underpressure in the surrounding airtight container by means of a pump. The air sampling flow rate is controlled by a critical orifice ($0.5 \text{ L} \cdot \text{min}^{-1}$) and the odor bag is thus filled in two hours time. In this way fluctuations in the composition of the air sample are time-averaged over two hours. A filter (pore diameter: $1 - 2 \mu\text{m}$) at the inlet of the sampling tube prevents the intake of dust that otherwise will contaminate the olfactometer. The sampling system is equipped with a heating system to prevent condensation in the bag or in the tubing. An odor bag remains in the container until analysis in the odor laboratory, which has to take place within 30 hours after sample collection. Odor concentrations are determined in compliance with the European olfactometric standard EN13725 (CEN, 2003) and the preceding Dutch olfactometric standard NVN2820/1A (NNI, 1996) that has been incorporated in the European standard. In both standards, the sensitivity of the odor panel is based on the 20 - 80 ppb n-butanol range. The odor concentrations are expressed in European Odor Units per m^3 air ($\text{OU}_\text{E} \cdot \text{m}^{-3}$) (CEN, 2003).

Dust (PM_{10}) measurement

The PM_{10} concentration of the biotrickling filter inlet and outlet air was measured gravimetrically. During a period of 24 hours a constant-air flow pump (TCR Tecora SRL, Milan, Italy; type: Charlie HV) sucked sample air through the PM_{10} measurement device. After entering the sampling head, the air flows through a pre-separator unit where particles larger than $10 \mu\text{m}$ are removed from the air. Finally the air passes through a filter holder containing a glass fiber filter ($\varnothing 47 \text{ mm}$, type GF-3, Macherey-Nagel, Düren, Germany) where the remaining PM_{10} fraction is accumulated the filter. For pre-separation a cyclone pre-separator (URG corp., Chapel Hill, USA; type: URG-2000-30ENB; sample air flow rate: $1.0 \text{ m}^3 \cdot \text{h}^{-1}$) was used. The cyclone pre-separator is used because the high dust load at animal houses may result in overloading when an impaction plate pre-separator is used (Zhao et al., 2009), which is the EU reference sampler for ambient air (CEN, 1998, 2005). During sampling, a moisture collection vessel for condensed water was located between the pump and the cyclone dust collector to protect the mechanics and electronics of the pump. Both the dust-free filters (before sampling) and the dust-loaded filters (after sampling) were weighed according to the European standard EN 14907 (CEN, 2005). From the weight difference between the dust-free and the dust-loaded filter, and the sample air flow at standard conditions, the 24-hour average PM_{10} concentration of the sampled air was calculated.

Nitrous oxide measurement

For the air sampling for the determination of nitrous oxide concentrations, the same procedure was used as for the odor measurements, although in this case a 24-hour sampling period was applied. The N_2O concentration in the bag was determined in duplicate with a gas chromatograph (Carbo Erba Instruments, GC 8000 Top; column: Haysep; detector: ECD/HWD).

Ventilation rate measurement

During the 24-hour measurements, the airflow rate through the biotrickling filters was measured continuously with measuring fans (location #1 and #3) or by means of a CO_2 balance method (location #2) (Pedersen et al., 2008).

RESULTS AND DISCUSSION

Removal performance for ammonia, odor and PM₁₀

In Table 2 the average inlet concentrations, removal efficiencies and empty bed air residence times (EBRTs) are shown for the three biotrickling filters.

Table 2. Removal performance of biotrickling filters treating exhaust air of animal houses, average values.

Location	NH ₃ -inlet (ppm)	NH ₃ removal (%)	Odor (OU _E .m ⁻³)	Odor removal (%)	PM ₁₀ (mg.m ⁻³)	PM ₁₀ (%)	EBRT (s) ¹
#1	12 (n=5)	85 (n=5)	1541 (n=6)	21 (n=6)	2.6 (n=6)	60 (n=6)	0.71 (n=6)
#2	7.2 (n=6)	71 (n=6)	1432 (n=6)	32 (n=6)	2.1 (n=6)	38 (n=6)	3.0 (n=6)
#3	29 (n=7)	86 (n=7)	1881 (n=7)	48 (n=7)	0.35 (n=7)	69 (n=7)	3.6 (n=7)

¹Defined as the packing volume (m³) divided by the airflow rate (m³.s⁻¹) during the measurements.

From Table 2 it follows that concentration levels and removal efficiencies are similar to the findings of other studies that were carried out at animal houses (e.g. Melse et al., 2005, 2012b). Furthermore, in Table 3 the inlet and outlet concentrations for N₂O are given and the N₂O production is compared with the NH₃ inlet.

Table 3. Removal performance of biotrickling filters treating exhaust air of animal houses, average values.

Location	N ₂ O-inlet (ppm)	N ₂ O-outlet (ppm)	N ₂ O-N production (% of NH ₃ -N inlet)
#1	0.31 (n=5)	1.1 (n=6)	13 (n=5)
#2	0.60 (n=6)	2.9 (n=6)	41 (n=6)
#3	0.55 (n=7)	4.3 (n=7)	24 (n=7)

From Table 3 it follows that N₂O concentration increases for all three biotrickling filters. This means that a significant amount of the inlet NH₃-N is not leaving the system as NO₂⁻ (aq), NO₃⁻ (aq), or N₂ (g), as was intended, but is converted to N₂O (g). On average 26% of the NH₃-N is converted to N₂O-N for the three biotrickling filters. This is much higher than a biotrickling filter system without denitrification where about 1-5% of the NH₃ is assumed to be converted to N₂O. In Table 4 the average composition of the water in the recirculation tank is given.

Table 4. Characteristics of water from recirculation tank, average values.

Location	pH	EC (mS.cm ⁻¹)	NH ₄ ⁺ -N (mg.L ⁻¹)	NO ₂ ⁻ -N (mg.L ⁻¹)	NO ₃ ⁻ -N (mg.L ⁻¹)	N-total (mg.L ⁻¹)
#1	7.0 (n=6)	6.8 (n=6)	0.93 (n=6)	0.23 (n=6)	0.12 (n=6)	1.4 (n=6)
#2	7.2 (n=6)	3.6 (n=6)	0.14 (n=6)	< 0.03 (n=6)	0.11 (n=6)	0.32 (n=6)
#3	7.8 (n=7)	18 (n=7)	1.8 (n=7)	1.2 (n=7)	0.27 (n=7)	3.6 (n=7)

Table 4 shows that the N-total concentration for location #2 < location #1 < location #3. The concentration levels for location #3 are similar to biotrickling systems without denitrification.

Nitrogen balance

In order to further understand the ammonia removal process in the biotrickling filter system, a nitrogen balance was established that takes into account both N-fluxes of water and air (Figure 2). For filter #2 a balance could not be established as no measurements of the discharge water flow were available. The difference between the total nitrogen input and output (Figure 2: "Unaccounted") might either be caused by measurement errors or by nitrogen sinks or emissions that have not been determined, e.g. the production of N₂ as a result of denitrification. Although the NH₃ removal efficiency of the systems is almost equal (see Table 2) large differences exist between the balances. Assuming that the unaccounted nitrogen is mostly N₂, biotrickling filter #1 is quite successful as a denitrification system as 63 + 15 = 78% of the inlet nitrogen is eventually denitrified. In biotrickling filter #3, however, only 32 + 24 = 56% of the inlet nitrogen is denitrified, in combination with a much higher N₂O production.

As a result, also the amount of discharge water of system 3 is higher, although the N content of the discharge water is higher than for system 1 (see Table 4). As a result of the occurring denitrification all installations were successful in reducing the amount of discharge water, as compared to regular biotrickling systems without denitrification, which was the aim of the air filter supplier.

It is known from literature that process parameters of denitrification systems influence the formation of N_2O . E.g. a too high O_2 concentration, a high nitrite concentration, and a too high nitrogen/organic matter ratio might result in an increase of N_2O production (Schulthess et al., 1994; Kampschreur et al., 2009; Temmink, 2008). Unfortunately, no further information on these process parameters is available for the three biotrickling filter systems that were monitored, except for the nitrite concentrations that were reported in Table 4.

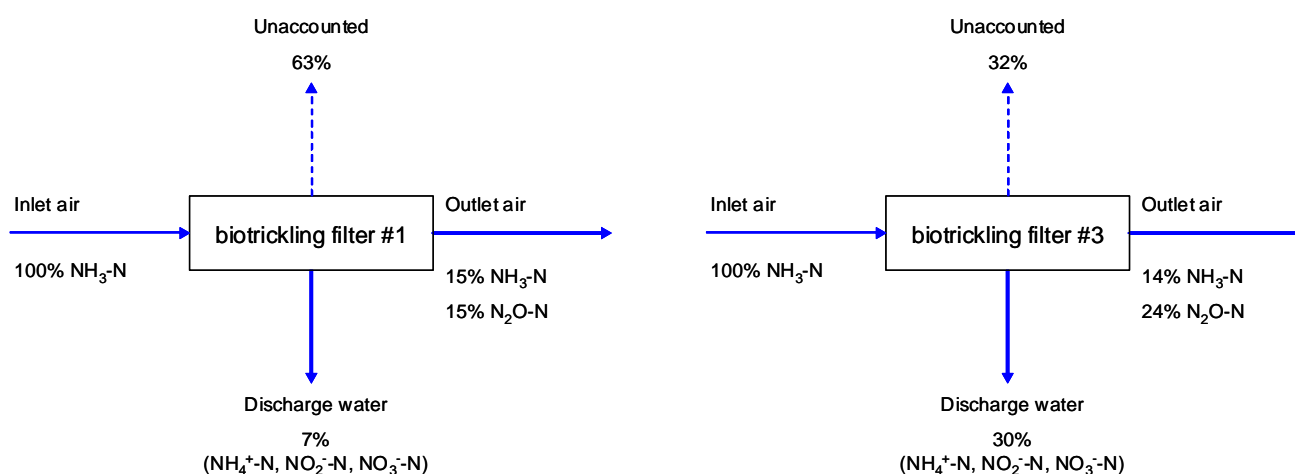


Figure 2. Nitrogen balance of two biotrickling filters treating exhaust air of animal houses. Inlet NH_3 -N amounts to 152 g.h^{-1} for filter #1 and 1059 g.h^{-1} for filter #3.

CONCLUSIONS AND RECOMMENDATIONS

It was found that the production of N_2O from the three biotrickling filters with denitrification system was quite high, on average 26% of the NH_3 -N was converted to N_2O . This is much higher than a biotrickling filter system without denitrification where about 1-5% of the NH_3 -N is assumed to be converted to N_2O -N. As the emission of N_2O , a potent greenhouse gas, is undesirable, further research is necessary to understand and explain the large differences in N_2O production that were found between the installations and to explore how process conditions can be adjusted in order to reduce the production of N_2O at these and other similar operated sites. Optimizing process conditions in practice might be quite a challenge as air treatment installations built at livestock facilities are usually relatively cheap and simple of design, as compared to installations that are built at industrial sites, which means that comprehensive process monitoring and control is usually absent. Currently, we feel that suppliers and municipality officials should be reluctant to install and permit this type of installations at livestock facilities because of the high N_2O emission that was found in this research.

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